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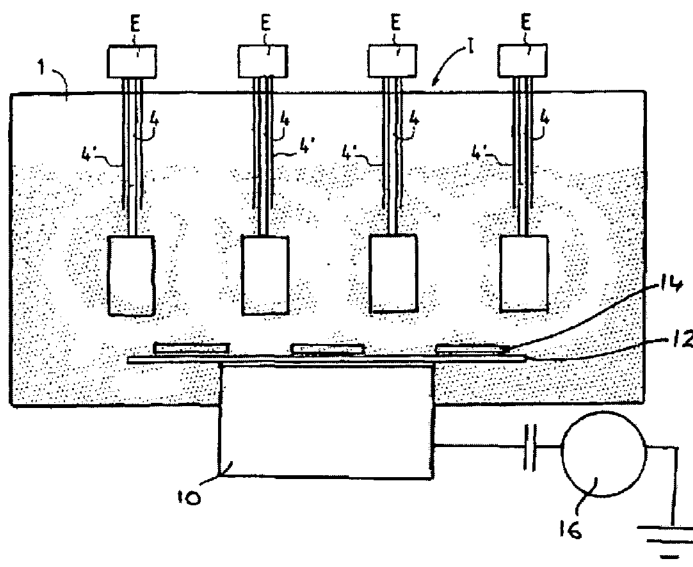

(57) Abstract: A method is described of forming a film of an amorphous material on a substrate (14) by deposition from a plasma. The substrate (14) is placed in an enclosure, a film precursor gas is introduced into the enclosure through pipes (20), and unreacted and dissociated gas is extracted from the enclosure through pipes (22) so as to provide a low pressure therein. Microwave energy is introduced into the gas within the enclosure as a sequence of pulses at a given frequency and power level to produce a plasma therein by distributed electron cyclotron resonance (DECR) and cause material to be deposited from the plasma on the substrate. The frequency and/or power level of the pulses is altered during the course of deposition of material, so as to cause the bandgap to vary over the thickness of the deposited material.

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FILM DEPOSITION OF AMORPHOUS FILMS WITH A GRADED BANDGAP BY ELECTRON CYCLOTRON RESONANCE

resonance

5 This invention relates to a method for forming a film of an amorphous material by deposition from a plasma on to a work surface. More particularly, it concerns the use of microwave energy to produce the plasma by electron cyclotron resonance. One area of particular interest is in depositing a film of amorphous silicon (a-Si:H) by dissociation of a silane, for example SiH_4, Si_2H_6 or a higher order of oligomer, in a
10 process known as plasma-enhanced CVD (chemical vapor deposition). Other precursor gases which can be used to deposit amorphous silicon, or amorphous silicon alloys, include molecules in which silicon is present in combination with one or more carbon, oxygen, or nitrogen, optionally together with hydrogen. An example of a silicon alloy is a structure of the type denoted by SiO_xN_y. Further, silicon-containing
15 gases may be used together with other gases, for example germane, or gases not containing silicon may be used to deposit other films, for example amorphous germanium or amorphous carbon. One area of particular interest as regards the use of amorphous silicon films in is devices for converting solar energy into electrical power. Such amorphous silicon material can also find use in electronic applications
20 such as TFT for display. As used herein, the term "amorphous silicon" denotes hydrogenated amorphous silicon, a-Si:H. For use in the areas just mentioned, some hydrogen must be present, typically 3-20%, to passivate the dangling bonds are defects.

25 In the technical field of exciting a plasma to electron cyclotron resonance (hereinafter abbreviated to "ECR"), resonance is obtained when the frequency of gyration of an electron in a static or quasi-static magnetic field is equal to the frequency of the applied accelerating electric field. This resonance is obtained for a magnetic field B at an excitation frequency f which is related to B by the following relationship:
30

$$B = 2\pi m f / e \qquad (1)$$

wherein m and e are the mass and the charge of an electron.

When exciting a plasma at electron cyclotron resonance frequency electrons revolve in phase with the electric field and continuously gain energy from the external excitation source where the ECR condition (1) is met such as to reach the threshold energy necessary for dissociating or ionizing the gas. To satisfy this condition, it is necessary firstly that the electron remains trapped in the magnetic field lines, i.e. that its radius of gyration is small enough with respect to the static magnetic field gradient for the electron to see a substantially constant magnetic field during its gyration, and secondly that the frequency of gyration remains large relative to the frequency of collision between electrons and neutral elements such as atoms and/or molecules. In other words, the best conditions for exciting a plasma to electron cyclotron resonance are expected to be obtained when simultaneously the gas pressure is relatively low and the excitation frequency f is high, which also means that the magnetic field intensity B must be high.

A major difficulty with conventional divergent ECR is that it is not possible to produce a plasma whose density is substantially uniform over a large area. This means that it cannot be used, for example, to deposit a substantially uniform layer of material on a work surface of large size. To overcome this problem, a technique has been developed which is known as distributed electron cyclotron resonance (DECR), which employs an apparatus in which a plurality of plasma excitation devices is formed into a network, with the devices collectively generating a plasma whose density is substantially uniform at the work surface. The individual plasma excitation devices are each constituted by a wire applicator of microwave energy, having one end connected to a source for producing microwave energy and having an opposite end fitted with at least one magnetic dipole for creating at least one surface having a magnetic field that is constant and of an intensity corresponding to electron cyclotron resonance. The dipole is mounted at the end of the microwave applicator in such a manner as to ensure that electrons accelerated to electron cyclotron resonance oscillate between the poles so as to create a plasma diffusion zone situated on the side of the dipole that is remote from the end of the applicator. The individual excitation devices are distributed relative to one another and in proximity with the work surface so as to create together a plasma that is uniform for the work surface.

Such a DECR apparatus is described in US Patent No. 6,407,359 (corresponding to EP-1075168), and more detailed discussion of the apparatus described therein is given below, with reference to drawings. As is apparent from those drawings, excitation devices, as viewed from the substrate, take the form of a generally rectangular array, by which we include the particular case where the rectangle is a square, and such an apparatus is therefore sometimes referred to as matrix DECR (MDECR) apparatus. It is to be understood, however, that the present invention could also be applied to a DECR apparatus where the excitation devices were arranged in a non-rectangular two-dimensional network, for example a hexagonal network or where there are two parallel lines of devices, with the devices in one line being offset with respect to one another. An example of a hexagonal array is given in "Determination of the EEDF by Langmuir probe diagnostic in a plasma excited at ECR above a multipolar magnetic field", T. Lagarde, Y. Arnal, A. Lacoste, J. Pelletier, Plasma Sources Sci. Technol. 10, 181-190, 2001. The devices could also be disposed as a circular, part-circular, or near-circular array. It should be noted that, in some work done by the present inventors, depositions have been carried out with a central plasma excitation device being surrounded by three or six devices, the surrounding devices having the polarity of their magnets being oppositely disposed to the magnet of the central device and being arranged in a triangular or hexagonal array respectively. Furthermore, the invention can be applied to a DECR apparatus which is not of an MDECR type. Thus, for example, it is applicable to a DECR reactor which, historically, preceded the MDECR type, and which has a cylindrical shape and uses long antennas and magnets that extend from the top to the bottom of the cylinder. Such arrangement is described in "Microwave Excited Plasmas" by Michel Moisan and Jacques Pelletier, Elsevier, 1992, and would be suitable for homogeneously coating a cylindrical substrate such as a tube but also a flat surface lying in the central part of the plasma and oriented perpendicular to the axis of the cylinder.

A thin film solar cell typically comprises an intrinsic layer (an i-layer) of an amorphous material, for example based on silicon, sandwiched between a p-doped layer (p-layer) and a n-doped layer (n-layer), and it is known that the conversion efficiency of the solar cell depends on, amongst other things, the bandgap of the amorphous material. Where the amorphous material has a constant bandgap throughout its thickness, a small bandgap provides larger sunlight collection and

hence larger conversion efficiency. However, it is also known that an advantageous structure can be obtained if the bandgap varies in an appropriate fashion over the intrinsic layer thickness. This is known as a graded bandgap. By way of further background to the present invention, there is now set out below a discussion of the
5 role of bandgap in solar cells, and why a graded bandgap may be valuable. It is to be understood that although the ensuing discussion focuses on an intrinsic layer in which there are a substantial number of layers of differing bandgap, the invention is also applicable to the case where there are just two layers differing in bandgap to one another, for example where most of the intrinsic layer is of constant bandgap and
10 there is a relatively thin layer of different bandgap adjacent either the p-layer or n-layer, for example a buffer layer of higher bandgap adjacent the p-layer. In addition the intrinsic layer can be made of two or more regions, not all of the regions having a graded bandgap structure. It is also to be noted that although the specific examples of the invention given below involve the deposition of a finite number of discrete layers,
15 with a step change in bandgap from one layer to the next, the invention is also applicable to a method in which the bandgap changes steplessly through all or part of its thickness.

As indicated above, the active part of thin film solar cells made of Si material includes
20 three layers: the p-doped layer, the intrinsic layer and the n-doped layer. As presented in the energy band diagram of Figure 10, the presence of the p and n-doped layers at the extremities of the intrinsic layer distorts the conduction and the valence bands and creates an electrical field. The holes (present in the valence band) drift toward the p-doped layer while the free electrons (present in the conduction band) drift toward the
25 n-doped layer.

It is well known that the mobility and the lifetime of the holes are significantly lower than for the electrons. In particular, the mobilities are 0.01 and 1 $cm^2/V/s$ respectively for holes and electrons in good a-Si:H material. Thus, when an electron-hole pair is
30 generated far from the p-layer, holes collection becomes critical. Therefore, grading the intrinsic layer from a low bandgap material close to the p-doped layer to a large bandgap material close to the n-doped layer is very beneficial for the holes collection, due to the increased electric field driving the charge carrier collection, and hence is beneficial for the overall cell performance.

Consideration also needs to be given to the way in which light absorption by amorphous silicon varies with wavelength. Since a-Si:H light absorption decreases with wavelength, the blue light is absorbed much faster than the red. If the cell is illuminated through the p or the n-layer, the blue light is absorbed respectively close to the P/I or the N/I interface while the red light is more uniformly absorbed throughout the thickness of the intrinsic layer. Also, the optical absorption of the sunlight decreases when the bandgap increases because photons having an energy smaller than the bandgap cannot be absorbed by the material. Therefore, increasing the bandgap of the intrinsic material from the p-doped to the n-doped layer reduces the optical absorption, particularly in the yellow-red part of the sunlight spectrum. Accordingly, when illuminating the cell through the p-doped layer, fewer electron/hole pairs are generated in the second half of the intrinsic thickness in a graded gap cell as compared to a non-graded gap one. However, as explained above, this direction of grading increases the probability that the holes which are generated are then collected, and this can more than compensate for the fact that fewer holes are generated. When a cell is illuminated from the n-doped layer this same direction of gradient will still be advantageous, since it will still enhance the holes collection but also the light absorption will be better spread throughout the intrinsic layer depth, hence closer to the P/I interface than for non-graded cells illuminated from the n-layer.

Graded bandgap junctions are also of interest for multi-junction devices. In such devices, the different junctions are typically connected in series with each other (see Figure 12), and the junctions must then be tuned to have identical current. The front junction will absorb the shortest wavelengths and then have the largest bandgap while the back junctions will absorb the longest wavelengths and have smaller bandgap.

A review of the field of compositionally graded bandgap solar cells is provided in N. Rafat, S.E.-D. Habib, "The limiting efficiency of band gap graded solar cells" Solar Energy Materials & Solar Cells, 55 (1998) 341-361. Most of the studies reported were on $Ga_{1-x}Al_xAs$ material and on a-Si alloys, especially a-SiGe. Indeed, it is well known that a-SiGe:H material is characterized by a large number of defects due to the network mismatch between Si and the Ge atoms. The main result of the published

literature is that grading the band gap enhances the cell efficiency through enhancement of the collection of minority carriers and the reduction of surface recombination rates.

Different types of bandgap grading of the i-layer, for example linear profiling in asymmetric v-and u-form, have been studied in the art with respect to their influence on the solar cell parameters (see, for example, Foelsch, J.; Stiebig, H.; Finger, F.; Rech, B.; Lundszien, D.; Labertz, A.; Wagner. Conference Record of the IEEE Photovoltaic Specialists Conference (1996), 25th 1133-1136). The shape of the bandgap profile has a major effect on the cell performance as can be shown by displacing the location of the region of smallest gap along the axis of the intrinsic layer. The grading profile has a profound effect on both the fill factor and the open-circuit voltage. Optimum performance has been found for an asymmetric v-shape with a bandgap minimum close to the p-i interface, as shown in Figure 13.

Various methods have been proposed for making graded bandgap structures. Thus, for example, graded bandgap Si alloys are disclosed in GB-A-2083701. In these structures the bandgap of the Si material is graded by introducing at least one bandgap adjusting element (i.e. Ge, Sn, C or N).

Another prior art document which discusses graded bandgaps is V. Dalal, G. Baldwin, P. Garikepati, "Improvements in stability of a-silicon solar cells through the use of bandgap grading" Conference Record of IEEE Photovoltaic Specialists Conference (1993), 23rd 816-20. This explains that the well-known degradation of a-Si:H cells is a result of additional defects creation in the intrinsic layer upon light excitation. These additional defects have two consequences:

(i) They act has additional recombination centres, thereby reducing the lifetimes of the electrons and holes, and hence, reduce the diffusion lengths of these carriers.

(ii) They shift the field distribution in the cell, reducing the electrical field in the middle and increasing it slightly at the p and n interfaces of a PIN a-Si:H cell.

The second issue is solved in this reference with a graded bandgap structure. After the p-layer and the large bandgap a-SiC:H buffer, the a-Si:H intrinsic layer is deposited in 3 steps:

(i) A constant low bandgap (preferably 1.65eV) layer of 100-150nm is deposited at 350°C.

(ii) A graded bandgap region where the bandgap is changed to about 1.8eV over 120-150nm is achieved by lowering the deposition temperature by 100°C and increasing
5 the dilution ratio (i.e. H_2/SiH_4).

(iii) A constant bandgap intrinsic region of 100-150nm followed by the n-layer are both deposited at 275°C.

All the layers are deposited by RF triode glow discharge with the substrate being
10 isolated from the plasma by a grid. The deposition rate was very low (probably ~1 Å/s), making possible the drop of 100°C during 100nm of deposition. Such a drop is not possible with DECR because the deposition rate is of the order of 25 times faster, making it impossible to lose 100°C within one minute.

15 The Dalal et al reference quoted above also explains that the grading of the bandgap is beneficial for the stabilization of the cell efficiency. The reference quotes the degradation of a standard cell and a graded cell as being 27% and 20% respectively after 35 hours 7xSun (xenon) illumination.

20 The present invention arises from the discovery that when a DECR process is used to deposit a film of amorphous silicon the bandgap of the deposited material can be varied by pulsing the microwave power, and varying the frequency and/or power of the pulses. It has also been found that with the DECR process, the film deposition rate is not affected by the MW pulse frequency, if the latter is not less than about 10Hz.

25

Accordingly, the present invention provides a method of forming a film of an amorphous material on a substrate by deposition from a plasma, which comprises placing the substrate in an enclosure, continuously introducing into the enclosure a film precursor gas at a flow rate, and extracting unreacted and dissociated gas from
30 the enclosure so as to provide a low pressure in the enclosure, and introducing microwave energy into the gas within the enclosure as a sequence of pulses at a given frequency and power level, to produce a plasma therein by distributed electron cyclotron resonance (DECR) and cause material to be deposited from the plasma on the substrate, wherein the said frequency and/or power level is altered during the

course of deposition of material, so as to cause the bandgap to vary over the thickness of the deposited material.

It is to be noted that the reference to the bandgap being graded by varying the pulse
5 frequency and/or power is not intended to exclude the possibility that the grading effect produced by this means may be supplemented by additional grading produced by other mechanisms, whilst using a film precursor gas of constant composition. One such mechanism is described in our copending application filed on the same date as the present application and entitled "Method for forming a film with a graded bandgap
10 by deposition of an amorphous material from a plasma" (our reference G28333EP (European Patent Application No. 06301117.5)) where the bandgap is graded by varying the flow rate of a film precursor gas. It is also to be noted that the invention covers both the production of a film in which the bandgap varies though all or part of its thickness in one or more steps (by varying the flow rate in a stepped fashion), and
15 the case where the bandgap varies through all or part of the thickness of the film in a continuous, stepless fashion (by varying the flow rate in a continuous, stepless fashion).

The invention is further described below with reference to the accompanying
20 drawings, in which:

Figure 1 is a diagrammatical elevation view showing a plasma production apparatus as described and shown in EP-1075168, omitting the means for introducing and extracting gas, which are shown separately in Figure 3;

25

Figure 2 is a plan view of the apparatus of Figure 1;

Figure 3 shows one way of introducing gas into the apparatus and extracting gas from the apparatus;

30

Figures 4 to 10 are graphs, described in detail below, showing how various properties vary with pulse frequency, power and substrate bias.

Figure 11 is an energy band diagram of a solar cell illuminated through the p-layer;

Figure 12 is a schematic view of a multi-junction solar cell device; and

Figure 13 is a schematic view of an asymmetric bandgap profile for a solar cell.

5

Figures 1 and 2 show an apparatus for producing a plasma relative to a substrate on which a film is to be deposited. The apparatus comprises a sealed enclosure 1 represented diagrammatically and fitted with devices for admitting gas and for pumping gas out (not shown in Figure 1), that enable the pressure of the gas that is to
10 be ionized or dissociated to be maintained at a desired value which, for example, can be about 10^{-2} to 2×10^{-1} Pascals, depending on the nature of the gas and the excitation frequency. However, gas pressures less than 10^{-2} Pa (say down to 10^{-4} Pa, for example), or above 2×10^{-1} Pa (say up to 5×10^{-1} Pa, or even 1Pa or more) can be used. For example, pumping can be carried out by a 1600 l/s Alcatel Turbo-molecular
15 pump, which serves to extract gas from the enclosure.

Gas is admitted to the enclosure from an appropriate gas source, e.g. a cylinder of gas under pressure, under the control of a mass flow controller. The gas may, for example, comprise SiH_4 as a film precursor gas, or one of the other gases mentioned above in
20 relation to the deposition of amorphous silicon. In addition to the film precursor there may also be introduced a non-reactive diluent gas, such as He, Ne or Ar, a reactive gas, such as hydrogen, nitrogen or oxygen, or a dopant gas such as diborane, trimethyl boron or phosphine. Typically, any such other gases are introduced into the enclosure through the same port or ports as the film precursor gas, as a mixture therewith, but
25 they could be introduced separately. The gas feeding system should ensure the appropriate flow of gases, which typically ranged from 1 to 1000 sccm (standard cubic centimetre per minute), into the reactor.

The injection port for the gas generally consists of a single tube, or a plurality of
30 tubes, entering the deposition chamber. The tube, or each tube, if there is more than one, can be extended by a grid to ensure more even distribution of the gas inside the deposition chamber. Injection can be carried out anywhere in the reactor but it is preferred to direct the film precursor gas towards the substrate surface. As used herein, it is to be understood that the reference to the outlet being arranged to direct

gas towards the substrate surface covers not only the case where the gas is aimed directly at the substrate surface on which the film is to be deposited, but also any case where the said surface is wholly within an angle defined between a line extending from the outlet, in the direction of gas flow therefrom, and a line which is at right
5 angles thereto and passes through the outlet. Under such circumstances the gas flow emerging from the outlet will have a vector component towards all portions of the said surface.

One way of doing this, referred as "point" injection, is shown diagrammatically in
10 Figure 3. In this arrangement the film precursor is introduced through a pipe, or a plurality of pipes 20 (two are shown), each of which has its outlet 21 located between the hot electron confinement envelope, as herein defined (shown by a broken line) and the substrate surface, and directed towards that surface. Figure 3 also shows an exit 22 through which unreacted and dissociated gas is pumped out. Other features of Figure
15 3 are described below with reference to the apparatus shown in Figure 1. Other injection arrangements of particular interest are described in our copending application filed on the same date as the present application and entitled "Method and apparatus for forming a film by deposition from a plasma" (our reference G28331EP (European Patent Application No. 06301115.9)), which describes the relative merits
20 of various injection arrangements.

The plasma chamber is equipped with a substrate holder 10, which is shown as a fixed part of the apparatus. One function of the substrate holder is to heat the substrates to the required deposition temperature. This is typically between room temperature and
25 600°C, and in the case of the deposition of amorphous silicon is preferably in excess of 200°C, more preferably between 225°C and 350°C. The temperature being referred to here is the actual substrate temperature, as opposed to the nominal substrate temperature which may be measured by measuring the temperature of the substrate holder. The significance of the distinction is discussed further in our co-pending
30 application filed on the same date as the present application and entitled "Method for forming a film of amorphous silicon by deposition from a plasma" (our reference G27558EP (European Patent Application No. 06301114.2)) mentioned above.

A carrier plate 12, having thereon at least one substrate 14, and optionally a plurality of such substrates, is removably mounted on the holder 10, so that it can be brought into the chamber with substrates to be coated, and removed from the chamber with the substrates after they have been coated. However, alternatively the substrate can be
5 glued directly on the substrate holder, using a thermally conductive glue. This improves thermal contact between the substrate and the substrate holder, which is otherwise difficult to achieve under low pressure conditions. This is discussed further in our co-pending application filed on the same date as the present application and entitled "Method for forming a film of amorphous silicon by deposition from a
10 plasma" (our reference G27558EP (European Patent Application No. 06301114.2)) . In this case the holder, with its substrates, needs to be introduced into the enclosure prior to the deposition process, and removed from it afterwards. If gluing is not used, one way to try to improve the heating of the substrate is to precede the low pressure film deposition step by a step in which the enclosure is filled with gas at a relatively
15 high pressure (typically around 100-200 Pa). The high pressure gas provides thermal transfer across whatever gap may exist between the substrate and the heated holder, ensuring initial heating of the substrates. Another possibility is to place a thermally conductive carbon film between the substrate and the substrate holder. The substrate holder can be heated by circulating a hot fluid inside it, but heating could alternatively
20 be achieved by electrical heating resistors embedded in the substrate holder. Alternatively, however, it is possible to heat the substrates directly, for example by using infrared lamps.

Another function of the substrate holder is to allow polarization of the substrate
25 surface such as to control the energy of ions towards the substrate. Polarization can be achieved using either a source of RF voltage or using a DC voltage and requires the substrate holder to be electrically insulated from ground. Polarization is achieved by connecting the electrically insulated substrate holder to an appropriate RF or DC generator 16 with an adequate matching circuit in the case of RF polarization. When
30 depositing on an insulating substrate, or on an insulating layer previously deposited on a substrate (which may or may not be insulating), the use of an RF generator is preferred. When depositing on a conductive substrate or a conductive layer previously deposited on a conductive substrate, which may or may not be conductive, the bias can be applied by either an RF or DC generator with suitable electrical connection to

the substrate surface. In a specific embodiment an RF-bias was applied using a 13.56 MHz Dressler generator connected to the substrate holder via an automatic tuning box. Even when using an RF generator, the resulting bias on the substrate surface comprises a DC bias component, as a result of conditions in the plasma. An
5 explanation of how this occurs can be found, in the content of the description of a completely different plasma process, in Suzuki et al, "Radio-frequency based microwave plasma etching technique: A method to increase SiO_2 etch rate", J. Vac. Sci. Technol. B 3(4), 1025-1033, Jul/Aug 1985.

10 The plasma production apparatus I has a series of individual plasma excitation devices E spaced apart from one another and located in the proximity of the substrates, so as to operate together to create a plasma that is uniform for the substrates. Each individual plasma excitation device E comprises an elongate microwave energy applicator 4. Each applicator 4 has one of its ends connected to a respective
15 microwave energy source, which lies outside the enclosure 1. Alternatively, however, a single microwave energy source can feed microwaves to all the applicators 4, or there can be a plurality of energy sources fewer in number than the number of applicators. For example, an array of sixteen applicators can conveniently be fed by two 2.45 GHz microwave generators, each of 2kW maximum power, and each
20 feeding eight applicators via a power splitter and respective slug tuners. Each applicator 4 is advantageously in the form of a tube surrounded by a coaxial tube 4', thus enabling microwave energy to propagate to the free end thereof while avoiding radiating microwaves and avoiding microwave coupling between the applicators. In order to ensure proper transfer of the microwave energy into the plasma, each
25 applicator is preferably equipped with a matching device that minimizes, or at least reduces, the reflected power from the plasma excitation device.

Each microwave applicator 4 has its free end connected to at least one permanent magnet 5. Each magnet preferably has its magnetic axis parallel to the long axis of the
30 magnet itself. In one particular form of this arrangement all the plasma excitation devices have their magnets oriented in the same direction (a monopolar configuration). i.e. all their north poles are at the top and all their south poles are at the bottom, or vice versa. In another, some of each pole are at the top and some of each pole are at the bottom (a multipolar configuration). An example of the latter is an

array, where, viewed from one end as in Fig. 2, and passing along any given row or column of devices, one successively encounters poles of alternate polarity. Yet another example is where all the magnets in a given row (or column) have the same polarity, but the columns (or rows) are of alternative polarity. However, arrangements can also be used where the magnetic axes of the magnets are not parallel to the long axes of the magnets themselves, provided there are significant regions where the lines of the magnetic field are parallel to the propagation vector of microwaves. This is necessary in order to ensure the existence of significant regions where ECR damping can occur.

As already indicated, the present invention arises from the discovery that pulsing the microwaves, and thus pulsing the DECR plasma, leads to a modification of the quality of the deposited layer, and in particular that the material bandgap can be altered by modifying the frequency of the pulsed plasma, in addition to which it was discovered that the pulse frequency has very little effect on the deposition rate, provided the frequency is not less than about 10Hz.

The following is a description of experiments carried out to investigate the dependence of the bandgap of deposited material on the frequency and power of microwave energy supplied to a plasma generating and depositing reactor.

The reactor used was equipped with 16 plasma excitation devices, each comprising an antenna and magnet, with the devices arranged in 4 rows of 4 devices. The microwave power was capable of being delivered to the antennas continuously, or being pulsed at a range of frequencies and with different duty cycles. For the pulse microwave experiments described below, a 1.2 kW Sairem GMP 12KE/D generator was used. Only the 4 central antennas of the 4x4 antennas network were fed with MW, as the generator had insufficient power to feed more. The Sairem generator can operate in CW (continuous wave) and pulsed mode with a frequency up to 30kHz, which made possible to compare materials deposited in the same operating and equipment conditions except for the frequency. The power from the generator was split in four, using a power splitter, and fed to the antennas. The pulsed signal to drive the generator was supplied by a Hewlett Packard wave function generator operating in square wave mode.

Depositions were carried out using a 100sccm silane flow rate, two different values of microwave peak power (125W/antenna, 250W/antenna) and using a continuous RF feeding of the substrate holder to create a bias of ~ -60Volts. Depositions were carried
5 in CW and pulsed mode with the Sairem generator at frequencies ranging from 10 Hz to 30 kHz, with a duty cycle of 50%. Films were deposited on Corning 1737 glass.

Optical properties of the films were obtained from spectroscopic ellipsometry data, by the Tauc-Lorentz model, to deduce the material bandgap, the maximum value of the
10 imaginary part of the dielectric constant (hereinafter denoted as ε_i(max)), the film thickness and its surface roughness. For a description of how this can be done see A. Fontcuberta i Morral, P. Roca i Cabarrocas, C. Clerc, "Structure and hydrogen content of polymorphous silicon thin films studied by spectroscopic ellipsometry and nuclear measurements", PHYSICAL REVIEW B 69, 125307/1-10, 2004.
15

By pulsing the microwave power fed to DECR antennas at various frequencies of 10kHz and above, it was found that the bandgap of the deposited material could be correlated with the frequency of pulsing, most likely due to the change of the plasma composition as the MW pulse frequency is changed. Typically a film having a lower
20 material bandgap was obtained as compared to the CW mode and it was discovered that the extent of the bandgap modification was dependent upon the frequency of the pulse. This is illustrated in Figure 4 for two values of the MW peak power applied to the MW antennas.

25 To enable the results for the CW mode to be represented on the logarithmic graph, the CW mode was arbitrarily assigned a "frequency" of 10^{-1}Hz. The conditions used are set out in Table 1.

Table 1

	Peak Power per antenna (W)	*Injection mode*	*Substrate bias*
125W/Antenna, Vol Inj.	*125*	*Volume*	*Continuous RF*
125W/Antenna, Point Inj.	*125*	*Point*	*Continuous RF*
250W/Antenna, Vol Inj.	*250*	*Volume*	*Continuous RF*
250W/Antenna Point Inj.	*250*	*Point*	*Continuous RF*
250W/Antenna Point Inj. Pulsed bias	*250*	*Point*	*Pulsed RF, synchronized with MW pulse*

It will be seen from the third column of this table that the second, fourth and fifth conditions used point injection, i.e. as shown in Figure 3. The first and third conditions used an alternative arrangement known as volume injection, in which the film precursor gas is introduced through a tube which extends into the reactor from below and is directed upwardly.

The effect of the frequency on the bandgap is seen for both values of the MW peak power but a much wider range of bandgap values is achievable at higher MW power. Under our high power conditions a range of 0.14eV is covered between CW and 30kHz.

It should be highlighted that a bandgap of 1.75 eV can be obtained using a microwave peak power of 250Watt/per antenna and pulsing at 10 kHz. Such a low bandgap can also be obtained using a lower microwave power (125W/antenna) but under CW mode. Carrying on the "low" power deposition under pulsed mode allows further reduction of the material bandgap down to 1.7eV in these deposition conditions.

Hence combining the changes of both the MW pulse frequency and the power fed to the plasma makes it possible to achieve a much wider bandgap range. In the present conditions, this range is 0.18eV.

Working at an even lower MW power is possible and, as expected from the above data, a further decrease of the material bandgap is observed. This is illustrated in Figure 5 for a MW frequency of 10kHz.

Thus, combining variation of both the frequency and the MW power enables a much wider bandgap range to be achieved. Both these parameters can be changed, in either a continuous or stepwise manner, during the deposition of the film, to produce a graded bandgap, i.e. a bandgap which varies over the thickness of the film.

Besides the effect of the pulsed MW frequency on the material bandgap, other changes of the material properties are expected, for example in the hydrogen content, the SiH_2/SiH_x ratio, the density and the value of $\varepsilon_i(max)$.

It is known that there is a link between the bandgap of an a-Si:H film and its hydrogen content; a higher hydrogen content induces a larger bandgap. This effect of the hydrogen content is also seen, to some extent, with its bonding with silicon and in
5 particular the ratio between the $=SiH_2$ and the $\equiv SiH$ groups in the film. The ratio $=SiH_2/SiH_x$ (SiH_x = sum of all the silyl hydride groups in the film, i.e. = $-SiH_3$ + $=SiH_2$ + $\equiv SiH$) increases with the hydrogen content. Figure 6 above shows that indeed a lower SiH_2/SiH_x ratio is obtained when the MW pulse frequency increases (at high MW power) and/or when the power is decreased (at constant frequency).
10

The frequency and power effects are also visible with other film characteristics such as the density (reflected in the value of $\varepsilon_i(max)$) as shown in Figure 7.

Despite some scattering in the data, caused by a quite extensive roughness of the
15 surface for some films (the reason is unknown, but it may have been due to poor RF bias coupling), there are clear trends showing that the material density improves when operating at higher pulsed MW frequency, this effect being also modulated by the power injected in the plasma. As a matter of fact, a lower bandgap will result from a lower hydrogen content and hence a higher density of the material, which translates
20 into a higher value of the maximum value of $\varepsilon_i(max)$.

Not only are the MW pulse frequency and the MW power delivered to the plasma important parameters that control the bandgap of the deposited material, but such control has to be operated in other well controlled deposition conditions, particularly
25 as regards the substrate temperature and the bias applied to the substrate. In the experiments described above the temperature of the substrate was not varied but was around 200°C. As regards the substrate bias, this should also be controlled, preferably by means of the applied RF power, as it has also an effect on the material bandgap and density as shown in Figures 8 and 9. It can be seen that the bias should preferably
30 be in the -40 to -80V range to ensure control of the bandgap and also achieve a good material density. To control the DC bias of the substrate, the RF power has to be adapted to the MW power injected into the plasma. To ease such control, the RF

generator, used to bias the substrate, can be operated in constant DC bias mode rather than constant power mode.

Another key parameter to control when it comes to grade a bandgap, in particular when a precise bandgap profile is to be achieved, is the deposition rate. We have found that in our operating conditions, the deposition rate is only slightly affected by the MW pulse frequency over a wide range of frequencies, such that no correction for the deposition time is required when changing the frequency.

This is shown in Figure 10, and the details are also set out in Table 2. It can be seen that the deposition rate hardly changes with the deposition frequency and the standard deviation (1σ) in the 10Hz-30kHz range is always lower than 10%. Thus, correction for the deposition time is not essential.

Table 2

Reference	*<Deposition rate> 10Hz-30kHz range (A/s)*	*Standard deviation 10Hz-30kHz range (%)*	*CW deposition rate (A/s)*	*Deposition rate ratio*
125W/Ant, Vol inj	*18.4*	*7.8*	*24.9*	*0.74*
125W/Ant, Point inj	*17.2*	*8.4*	*23.8*	*0.72*
250W/Ant, Vol inj	*23.4*	*8.6*	*27.5*	*0.85*
250W/Ant, Point inj	*23.8*	*5.0*	*28.7*	*0.83*
250W/Ant, Point inj, Pulsed Bias	*24.2*	*3.9 (10Hz-1kHz)*	*na*	

When the CW mode is included in the deposition of the graded gap structure, a correction is however required to adjust the deposition time between the CW and the pulsed mode, as can be seen by the values of the deposition rate ratio, which is the deposition rate achieved at a particular frequency, divided by the deposition rate achieved under otherwise the same conditions but using the CW mode. Below 10Hz, the OFF time becomes longer than the characteristic lifetime of the plasma and the deposition rate decreases significantly.

Conclusions

It can be seen from the above that the bandgap of a film deposited by DECR-PECVD can be tuned by pulsing the MW power fed to the antennas. This can be achieved with a single film precursor gas and hence does not require the use of gap grading gases.

The material bandgap is controlled by both the frequency of the MW pulse as well as its power. For a given duty cycle (in our experiments this was 50%), increasing the pulse frequency results in a decrease of the material bandgap. Such decrease is also a function of the MW power. Under our operating conditions, when scanning the frequency from CW to 30kHz, the bandgap varied by 0.14eV and 0.04eV for MW powers of 250W/antenna and 125W/antenna, respectively. Further decrease of the injected power results in a further adjustment of the bandgap.

Hence by combining changes of both the MW pulse frequency and the MW pulse power, a fine tuning of the material bandgap can be achieved over a range which is in excess of 0.18eV.

Such changes can be made in a continuous or stepwise manner, so as to produce a single layer with a continuously changing bandgap or a stack of a plurality of layers, each having a different bandgap.

Bandgap grading can be made in any direction (wide to narrow or narrow to wide) and even take a V or U shape. An example of a V-shape bandgap, in fact an asymmetric V-shape, is shown in Figure 13.

The production of a layer having a continuously graded gap is helped by the fact that in the DECR mode the film deposition rate has been found to be hardly affected by the MW pulse frequency and does not require time correction to produce a constant slope graded gap.

A graded bandgap layer of amorphous material produced by the method of the invention, particularly amorphous silicon, can be used, for example, as the intrinsic layer in a solar cell. Either the intrinsic layer is deposited on a substrate of an n-doped material, and a layer of the p-doped material is formed on the film of amorphous material, or the intrinsic layer is deposited on a substrate of a p-doped material, and a layer of n-doped material is formed on the film of amorphous material.

CLAIMS:

1. A method of forming a film of an amorphous material on a substrate by deposition from a plasma, which comprises placing the substrate in an enclosure,
5 continuously introducing into the enclosure a film precursor gas at a flow rate, and extracting unreacted and dissociated gas from the enclosure so as to provide a low pressure in the enclosure, and introducing microwave energy into the gas within the enclosure as a sequence of pulses at a given frequency and power level, to produce a plasma therein by distributed electron cyclotron resonance (DECR) and cause
10 material to be deposited from the plasma on the substrate, wherein the said frequency and/or power level is altered during the course of deposition of material, so as to cause the bandgap to vary over the thickness of the deposited material.

2. A method according to claim 1, wherein the film deposited is hydrogenated
15 amorphous silicon.

3. A method according to claim 2, wherein the film precursor gas comprises a silicon hydride.

20 4. A method according to claim 3, wherein the film precursor gas comprises SiH_4.

5. A method according to claim 1, wherein the film deposited is an amorphous silicon alloy.

25

6. A method according to any preceding claim, wherein the plasma is produced by devices arranged to form a two-dimensional network.

7. A method according to claim 6, wherein the plasma is produced by matrix
30 DECR.

8. A method according to any preceding claim, wherein a plurality of layers are successively deposited on the substrate, each layer having a larger bandgap than the previous layer.

9. A method according to any one of claims 1 to 7, wherein a plurality of layers are successively deposited on the substrate, each layer having a smaller bandgap than the previous layer.

5

10. A method according to any one of claims 1 to 7, wherein the layers are so deposited as to cause the bandgap to have a minimum at a point spaced from both the first and last layers to be deposited.

10 11. A method according to any one of claims 1 to 7, wherein the bandgap of the film is caused to vary continuously and steplessly through all or part of its thickness, by varying the flow rate in continuous, stepless fashion.

12. A method according to any preceding claim, wherein the said frequency is at
15 least 10Hz.

13. A method according to any preceding claim, wherein only the frequency is altered.

20 14. A method according to any one of claims 1 to 12, wherein only the power is altered.

15. A method according to any one of claims 1 to 12, wherein both the frequency and power are altered.

25

16. A method according to claim 13 or 15, wherein during the course of deposition there is a stage during which microwave energy is supplied as a continuous wave.

30 17. A method according to any preceding claim, wherein the said flow rate is also altered during the course of deposition.

18. A method of making a solar cell, wherein a film of amorphous material is formed by the method of any preceding claim on a substrate of an n-doped material, and a layer of a p-doped material is formed on the film of amorphous material.

5 19. A method of making a solar cell, wherein a film of amorphous material is formed by the method of any preceding claim on a substrate of a p-doped material, and a layer of an n-doped material is formed on the film of amorphous material.

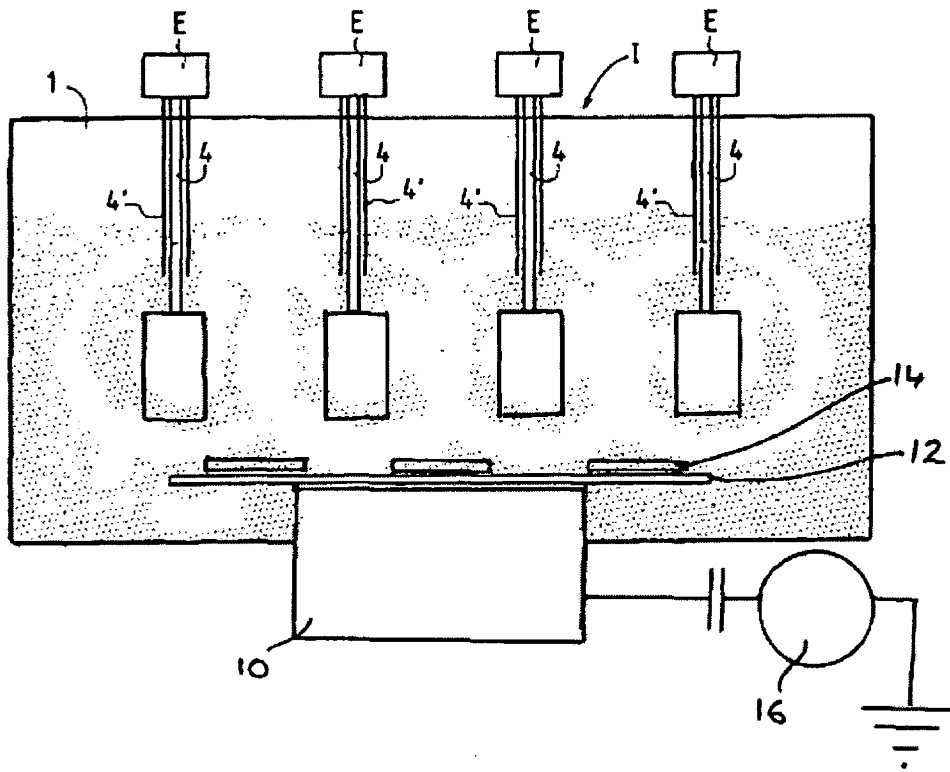

Figure 1

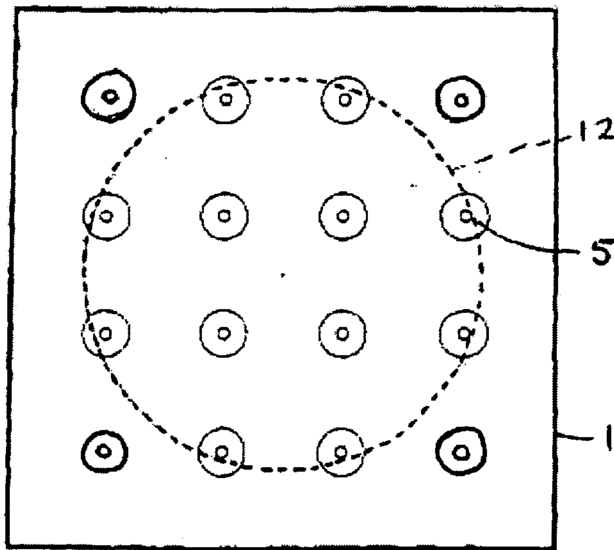

Figure 2

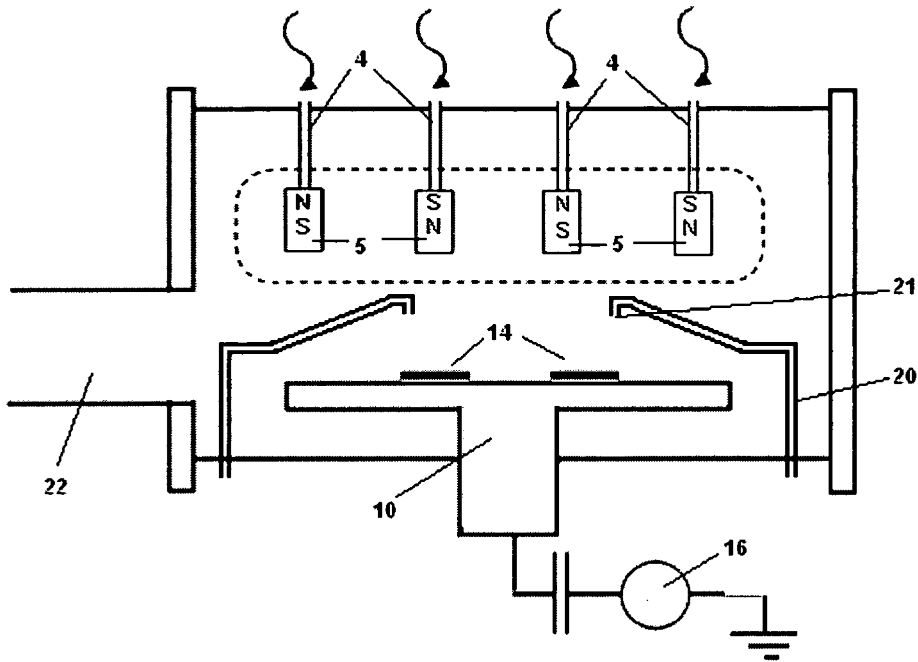

Figure 3

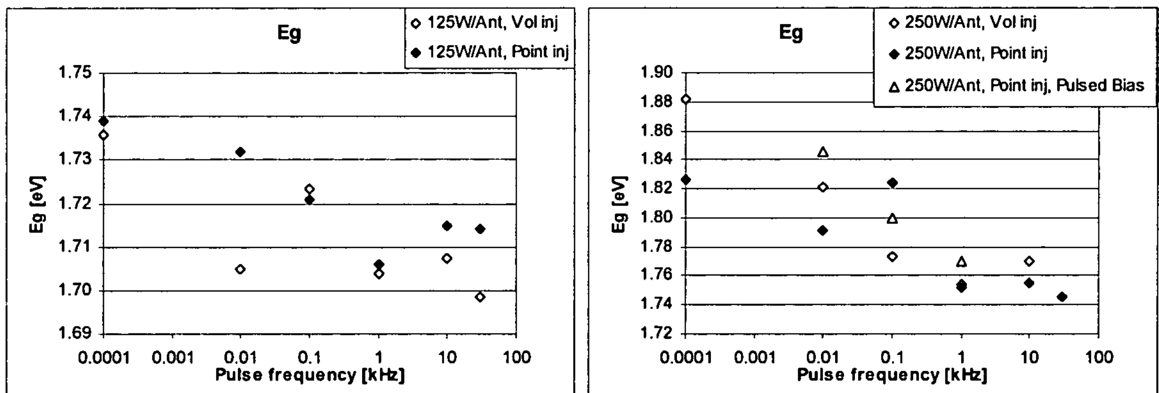

Figure 4

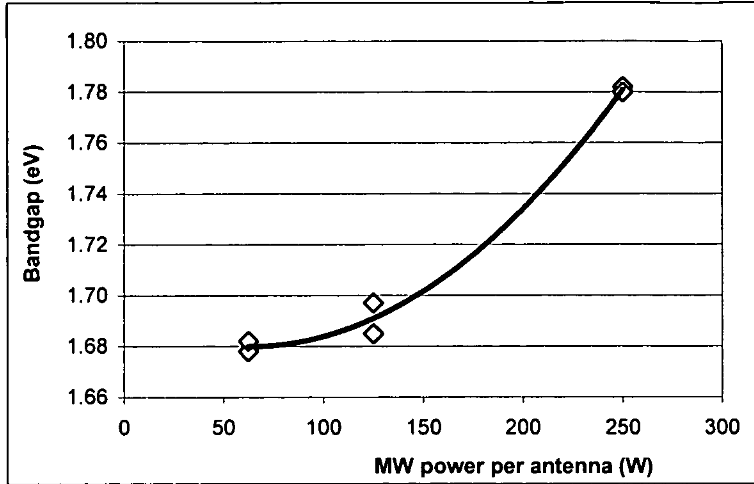

Figure 5

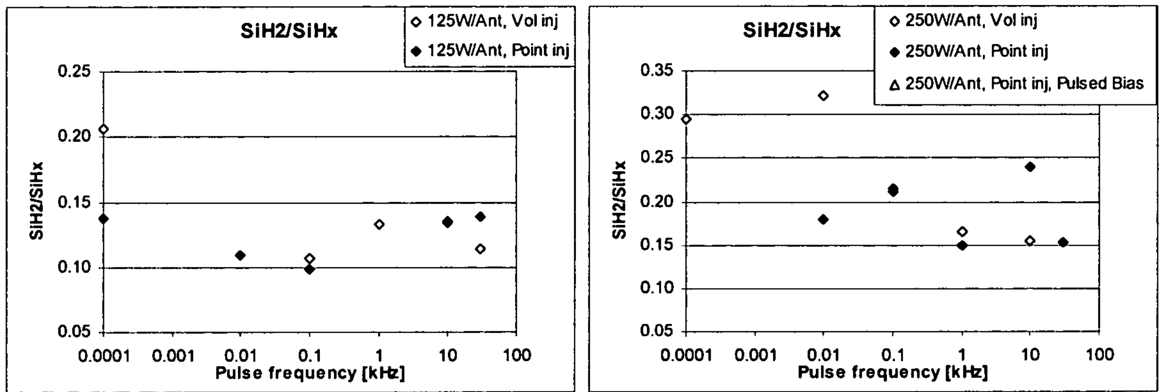

Figure 6

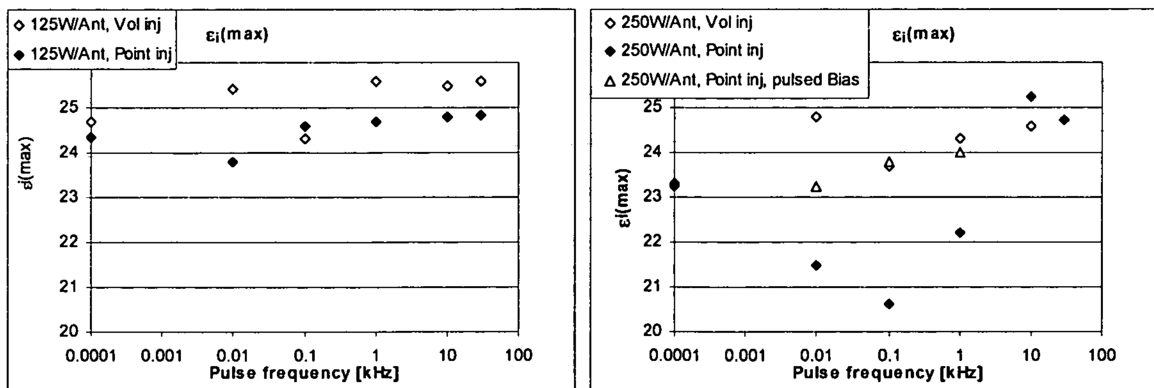

Figure 7

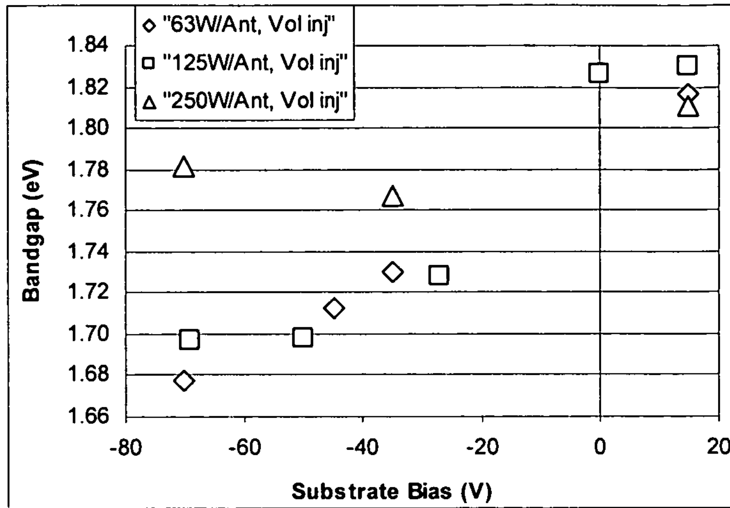

Figure 8

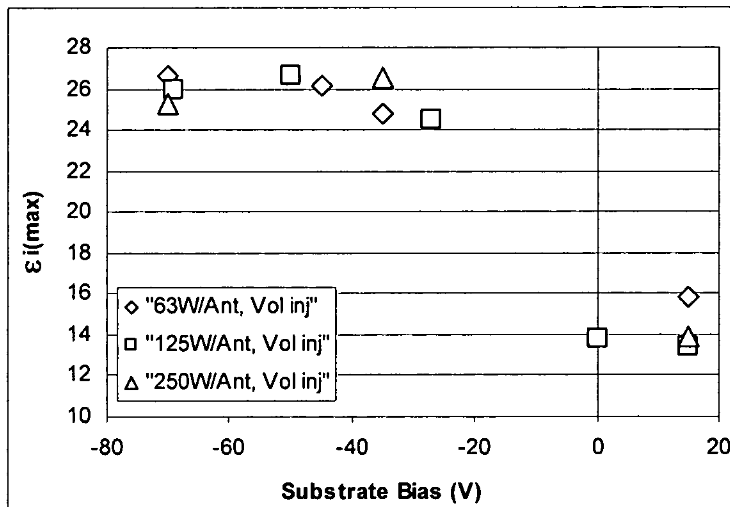

Figure 9

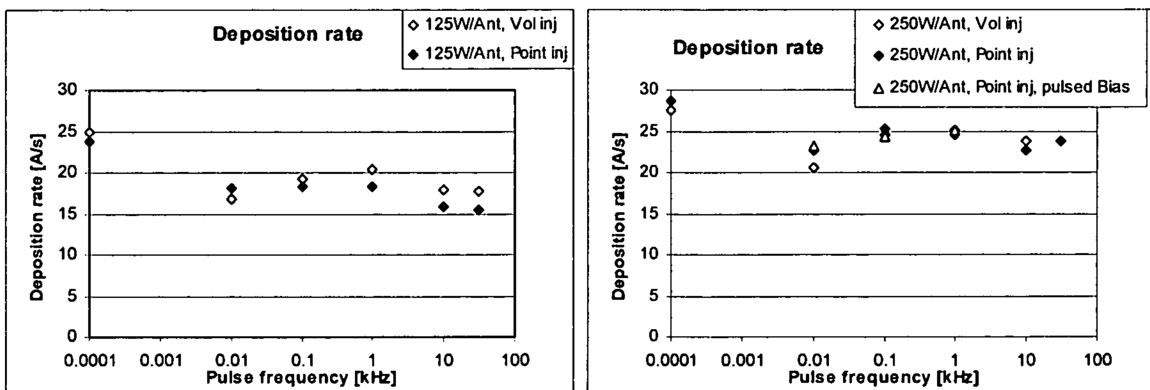

Figure 10

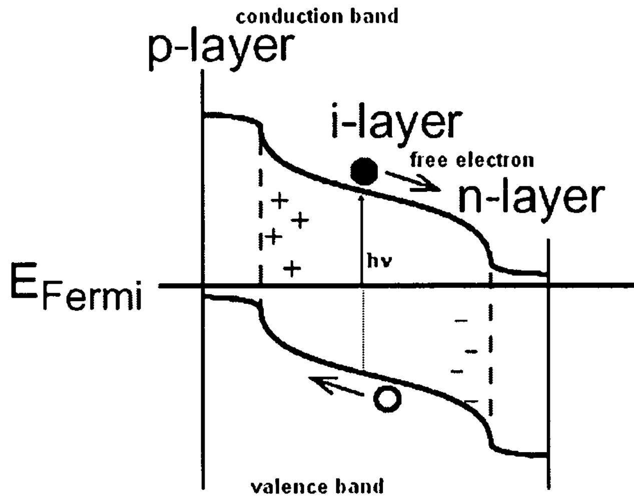

Figure 11

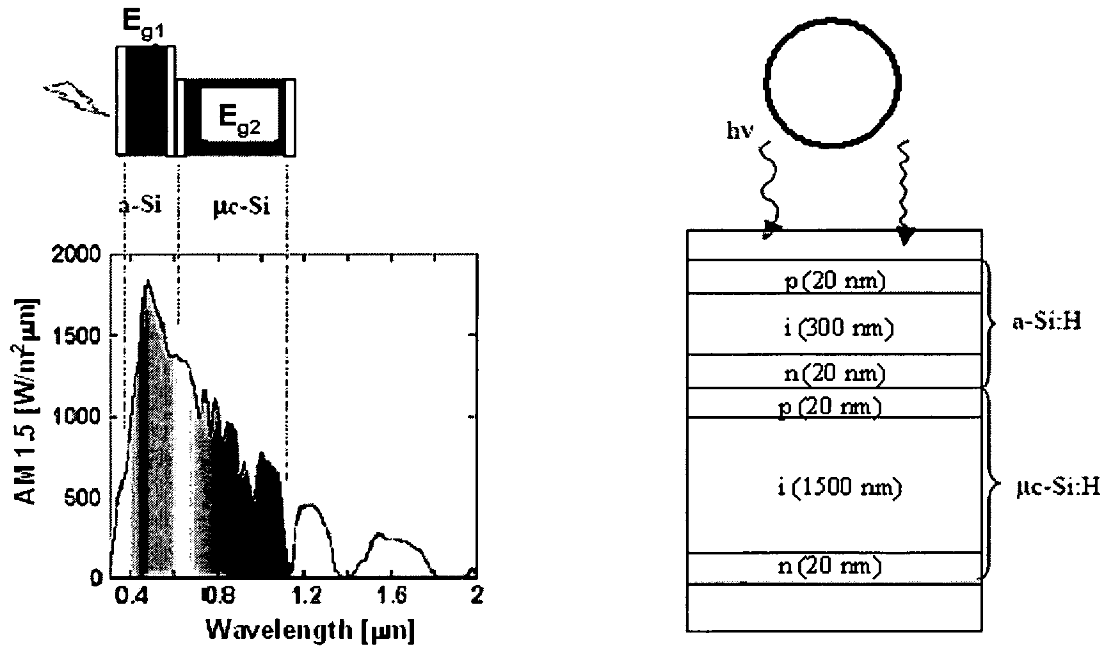

Figure 12

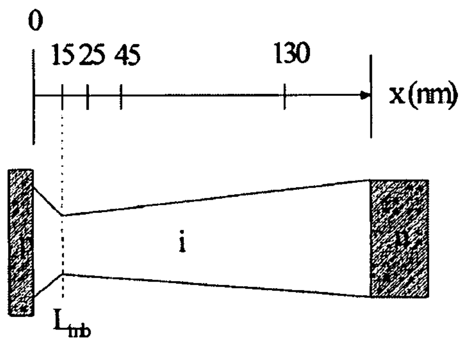

Figure 13

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/009307

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/24 C23C16/511 H01J37/32 H01L31/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C H01J H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/022349 A1 (SUGIYAMA SHUICHIRO [JP] ET AL) 21 February 2002 (2002-02-21) claims 1-4; figures 1-10; examples 1,2; table 1 -----	1-19
Y	DAINEKA D ET AL: "Control and monitoring of optical thin films deposition in a matrix distributed electron cyclotron resonance reactor" EUROPEAN PHYSICAL JOURNAL, APPLIED PHYSICS EDP SCIENCES FRANCE, vol. 28, no. 3, December 2004 (2004-12), pages 343-346, XP002436180 ISSN: 1286-0042 page 343, column 2, line 17 - page 345, column 2, line 6; figure 5 -----	1-19

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 November 2007	10/12/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lavéant, Pierre

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/009307

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002022349 A1	21-02-2002	JP 2001332749 A	30-11-2001